

1 BACKGROUND OF THE INVENTION:

2 This invention relates to a new and improved resin-  
3 impregnated fabric, which upon curing, is suitable for use as a  
4 wet friction material in transmission couplings, automatic  
5 lockers, limited slip differentials, smart clutches, brakes,  
6 synchronizers and the like. More particularly this invention  
7 concerns the use of woven or braided fabric utilizing continuous  
8 untwisted carbon filament yarn or other fiber, and impregnating  
9 this material with a modified cyanate ester oligomer at low  
10 concentration levels for such use after curing.

11  
12 The use of woven fabrics containing different resins such as  
13 phenolics, pyrolytic carbon, epoxy, etc., are well known in the  
14 industry and have been used for many years in the aerospace and  
15 automotive industries.

16  
17 Also, the use of resin-impregnated fabric cured composites  
18 as wet friction materials in transmission and brake components is  
19 well known, and typical publications concerning this use are  
20 disclosed in U.S. Patents 4,700,823; 5,662,993; 5,842,551;  
21 5,895,716; 5,952,249; 6,060,536; 6,132,877 and, 6,135,256. In  
22 wet friction applications, the flow of hydraulic fluid and the  
23 hydrodynamic film formed between the driven and non-driven member  
24 of the transmission play an important role in providing effective  
25 performance as transmission couplings.

1       The materials described in these patents may have various  
2 problems associated with their use. For example, in the case of  
3 U.S. Patent 5,662,993 to Winckler there is a problem with the  
4 type of fabric employed, which is woven with bundles of twisted,  
5 stretch-broken filaments. The problem arises since the loose  
6 strand ends described in those patents can become worn due to  
7 abrasion. Eventually these loose ends may tend to break off,  
8 causing contamination due to the formation of debris within the  
9 fabric which then becomes plugged; this debris tends to interfere  
10 with oil circulation.

11

12       Moreover, since the fabric material used in the Winckler  
13 patents is bulky, this bulkiness requires a fairly large amount  
14 of phenolic (or other) resin to be employed for effectiveness.

15

16       Also in the Winckler patent, the twisted bundles of  
17 discontinuous staple fibers in the fabric are made by stretch  
18 breaking, twisting and spinning, which is similar to cotton yarn  
19 production. However, this process of carbon staple yarn  
20 production is expensive. In addition, since the lengths of these  
21 discontinuous filaments can be in the range of about 1/4" - 4",  
22 the fabric formed from this fuzzy type of yarn does not produce  
23 the same strength as fabric formed from continuous, untwisted  
24 filament strands.

25

1        Phenolic resins have been in use for many years because  
2        their high cross linking density and high aromatic ring content  
3        results in a high glass transition temperature and a high char  
4        yield. However, because of their high cross linking density,  
5        phenolic resins tend to be more brittle and resemble crystalline  
6        materials which have poor adhesion to carbon fibers. Also,  
7        during the phenolic curing stage, some reaction by products are  
8        emitted which cause porosity and bulkiness.

9

10        THE INVENTION:

11        According to the invention, there is provided wet friction  
12        cured composite materials for use in torque converters such as  
13        transmission couplings, locking differentials, automatic lockers,  
14        limited slip differentials, smart clutches, synchronizers,  
15        brakes, and the like. The cured, composite materials comprise a  
16        modified cyanate ester oligomer impregnated fabric formed from a  
17        woven or braided fabric from continuous, untwisted filament yarn.

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19

20        Modified cyanate ester oligomers are preferred because of  
21        their unique cross linking and triazine ring formation which  
22        impart high glass transition temperatures and also function more  
23        like polymeric matrices with improved toughness and good adhesion  
24        to the carbon fiber.

25

1 Typical fabric materials include those woven from carbon,  
2 graphite, ceramics such as NEXTEL<sub>R</sub> (3M), aramid fiber, glass,  
3 quartz, silica, and mixtures thereof, and typical fabric weaves  
4 include plain, braided, 5 and 8 harness satin, basket, twill,  
5 crowfoot satin, or other suitable weaves. When used as a braided  
6 weave, the fabric can be formed as a continuous spiral, cut to  
7 size, and bonded to the transmission in one piece, rather than  
8 being bonded in segments as joints or discs cut from the fabric  
9 which are now being manufactured.

10

11 Preferred modified cyanate ester oligomers include  
12 multifunctional cyanate ester modified phenolic novolac resins  
13 sold by Lonza under the trade names of PT-15, PT-30 and PT-60.

14

15 Other possible modified cyanate ester resin types and  
16 oligomers are disclosed in the textbook entitled: "CHEMISTRY AND  
17 TECHNOLOGY OF CYANATE ESTER RESINS", edited by I. Hammerton,  
18 published by Blackie Academic and Professional, 1994, and which  
19 is incorporated herein by reference. Typical cyanate resin  
20 monomers which may be considered for use in the fabric material  
21 of this invention are listed in that text on pages 3, 35, 38, 39,  
22 40, 41, 42, 44, and 47 - 52, incorporated herein, by reference.

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1        Specific resins are selected based on a suitable combination  
2 of characteristics for transmission coupling requirements (but  
3 not limited thereto) such as high temperature performance,  
4 abrasion resistance, toughness and fabric compatibility.

5  
6        However, while a wide variety of fabric materials are also  
7 disclosed in that text, the possible combination of fabric,  
8 cyanate resin and resin weight, is not disclosed or inferred as  
9 a wet fabric material suitable for transmission coupling  
10 purposes. For example, pages 325 - 326, 331, and 343 of that  
11 text give no indication that a combination of fabric, cyanate  
12 resin and resin weight could be employed for transmission  
13 coupling purposes.

14  
15        The resin content in the cured fabric is estimated at least  
16 about 10% based on the cured weight of the resin and fabric, and  
17 may vary up to at least 40% - 50% for certain unique specific  
18 applications. Suitable resin content weights may include  
19 10% - 35%; and, 10% - 25%. The preferred resin weights are about  
20 10% - 18%, and most preferably about 12% - 17% of the cured  
21 weight of the resin and fabric combined for some automotive and  
22 truck applications. This considerably lowers the resin content  
23 in the fabric compared to the prior art.

1       Following impregnation of the fabric using a mixture of  
2 resin in a suitable solvent such as ketones, esters (e.g.,  
3 acetates), ethers, or miscellaneous solvents such as methylene  
4 chloride, dimethyl acetamide, monochlorobenzene, propylene  
5 carbonate, etc., the fabric is then cured. The cured composite  
6 is then coated with a slightly tacky adhesive film backed with a  
7 release paper, or the cured composite may be simply coated with  
8 an adhesive for direct application to a metal surface.  
9 Alternatively, the cured composite may be supplied without any  
10 surface adhesive coating, and the coating is applied at the  
11 transmission installation site.

12

13       When it is desired to install the impregnated and cured  
14 fabric material onto a transmission component, a primer is  
15 applied to the metal surface, and the fabric is placed with its  
16 adhesive side onto the surface of the transmission component.  
17 This combination is then heated under compression for about  
18 3 - 13 minutes, or as commercial efficiency times dictate,  
19 thereby further curing the cyanate resin, and at the same time  
20 bonding the fabric to the transmission component. This process  
21 also produces a suitable thickness of the cured fabric.

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1       The cured fabric thickness can vary widely such as from  
2   0.015 - 0.080 inches; and typically may vary from about  
3   0.020 - 0.030 inches, and preferably from about 0.024 - 0.028  
4   inches. If desired, two or more cured fabric layers may be  
5   adhesively bonded together to produce a greater thickness. The  
6   number of ends in the filament yarn may vary from about  
7   1000 - 24,000, and typically are about 6,000.

8  
9       Bonding of two carbon fabric layers together was  
10   accomplished by applying a primer layer to an adhesive film  
11   between two layers of fabric which were then heated in a press at  
12   425°F and 100 psi for six minutes. After cooling, the material  
13   of the two layers was well bonded together, and the outer sides  
14   had the same texture as a single layer material.

15  
16       In a second experiment, a primer was painted onto a thin  
17   fiberglass matt (about 1 mil) and this matt and adhesive film  
18   were placed between two cured carbon fabric layers and then  
19   bonded under the same conditions, as previously noted. The  
20   thickness of the single layer was 0.024 - 0.028 inches, and that  
21   of the two layers bonded together was 0.048 - 0.054 inches.  
22   Other techniques for bonding the two layer of cured fabric could  
23   be used.

24  
25

1 Phenolic resins due to low cost, flame resistance and high  
2 glass transition temperatures have a long history of use in the  
3 composite industry. However, it is well known that their  
4 adhesion and shear strength on carbon fiber is fairly low. To  
5 illustrate this point a cured swatch of stretch broken twisted  
6 carbon fabric impregnated with a phenolic resin such as Aerofene  
7 295 available from Ashland Chemicals was compared with the same  
8 cured fabric with a cyanate ester oligomer based swatch of Pt-30  
9 available from Lonza Chemicals.

10  
11 EXAMPLE 1. A solution of a phenolic resin (Aerofene 295 obtained  
12 from Ashland Chemical) was further diluted with isopropanol, and  
13 the resulting solution was used to prepreg a swatch of plain  
14 weave stretch broken twisted yarn carbon fabric. Following  
15 devolatizing, the prepreg material was cured.

16  
17 EXAMPLE 2. To an acetone solution of a polycyanate of a novolac  
18 phenol resin (PT-30) there was added 2 grams of copper acetyl  
19 acetate in nonyl phenol. The resulting solution was used to  
20 impregnate a 12 x 12 swatch of the fabric described in Example 1.  
21 After devolatizing to achieve cross linking, the prepreg was oven  
22 cured for two (2) hours at 350°F followed by a post cure at 425°F  
23 and 550°F.



1       A simple test was performed by rubbing an eraser over both  
2 the cured fabrics of examples 1 and 2 for comparison purposes,  
3 and it was found that more broken filaments were produced from  
4 example 1, compared to example 2. This would suggest that  
5 cyanate resins will have less contamination problems when used  
6 for transmission purposes, and also that the cyanate ester-based  
7 cured material seemed to have better adhesion to the stretch-  
8 broken plain weave carbon fabric compared to the phenolic resin.

9  
10       While unmodified cyanate ester polymers are generally  
11 tougher than unmodified phenolic resins, with proper modification  
12 the toughness of cyanate resins can be improved without  
13 sacrificing temperature performance. For example, it has been  
14 well documented that adding certain thermoplastics to cyanate  
15 ester resins will increase the matrix toughness without adversely  
16 affecting the modulus or the glass transition temperature.  
17 Several thermoplastics which are compatible with poly-m-methyl-  
18 phenylene cyanate oligomers and other cyanate esters include  
19 polyether sulfone; polyphenylene oxides; polycarbonates; epoxy  
20 thermoplastics; and, polyimide polymers.

1 Cyanate ester oligomers modified with silicone based  
2 reactive or non-reactive elastomers may be particularly useful in  
3 order to achieve abrasion resistance and lower friction  
4 properties. These silicones include products such as  
5 polydimethyl silsesquioxane alkyl polyethoxy ethanol (Additive  
6 23), alkoxy polyethoxy ethanol and, dimethyl silicone resin  
7 (Additive 22); and General Electric's dimethyl polysiloxane with  
8 methylsilsesquioxanes (TPR 179), polydimethyl siloxane (TPR 178)  
9 with methylsilsesquioxanes silicone resins, and other methyl  
10 phenyl silicone resins.

11  
12 Modified cyanate ester resin and oligomers may include  
13 polycyanate resins modified with: epoxy resins; silicone  
14 elastomers; polycyanate resins modified with polyetherimide  
15 resins; polycyanate resins modified with polyphenoxy resins; and,  
16 polycyanate resins modified with: diglycidyl ethers of a novolac  
17 resin, and a polyglycidyl ether of a cresol novolac resin.

1       The following examples 3 - 6 utilize a continuous filament,  
2 carbon plain weave fabric where each bundle contains about 6,000  
3 continuous carbon filaments.

4  
5       **EXAMPLE 3.** A solution of a thermoplastic polyetherimide (ULTEM<sup>R</sup>  
6 sold by General Electric) having a glass transition of 420°F, was  
7 dissolved in methylene chloride and used to prepreg a swatch of  
8 carbon fabric. Following devolatizing and curing, the carbon  
9 fabric exhibited an increase in toughness. However, the glass  
10 transition temperature of the product was too low to enable its  
11 use as a transmission coupling.

12  
13       It will be appreciated that while transmission temperatures  
14 during normal operation are about 200°F - 250°F, when the non-  
15 driven member engages the driven member of the converter, the  
16 surface temperature of the facing material can spike for a  
17 fraction of a second to several hundred degrees Fahrenheit.  
18 These temperature spikes, require the matrix of the carbon based  
19 surfacing material to have a high glass transition temperature  
20 capability and toughness, and suitable matrices are given below.

1        While the use of some thermoplastics may be a viable choice,  
2        their glass transition temperatures are generally too low. By  
3        combining some of these thermoplastics with a cyanate ester resin  
4        or oligomer, an improvement in both the glass transition  
5        temperature and toughness of the matrix can be achieved, and this  
6        improvement is shown in example 4.

7  
8        **EXAMPLE 4.** To one part of a solution of ULTEM<sup>R</sup> (example 3), and  
9        ten parts P-30 (example 2), there was added a copper acetyl  
10       acetate catalyst. This solution was used to prepreg a swatch  
11       of carbon fabric, followed by devolatilizing and curing the  
12       prepreg, as in example 2. This product resulted in both the  
13       glass transition temperature and toughness being improved.

14  
15       While adding a polycyanate ester oligomer such as Pt-30 in  
16       conjunction with ULTEM in methylene chloride will solve the glass  
17       transition temperature problem and have the needed toughness, the  
18       use of chlorinated solvents makes this approach commercially less  
19       desirable.

20  
21       **EXAMPLE 5.** A solution of {phenol, 4,4'-(1-methylethylidene)  
22       bispolymer and (chlormethyl oxirane) phenoxy resin} - PKHH from  
23       Phenoxy Associates, was prepared in MEK. To 20 parts of this  
24       solution was added 80 parts of a solution of PT-30 (example 2),  
25       and a copper catalyst.

1       The combined solution was used to prepreg a swatch of carbon  
2 fabric and cured as in example 2. Actual road tests of  
3 transmissions employing continuous carbon fiber fabric with the  
4 resulting modified cyanate esters having resin contents ranging  
5 from 12% - 17% confirmed the excellent performance of these  
6 materials.

7  
8       Another acceptable approach utilizes a mixture of Pt-30  
9 cyanate ester oligomer in combination with diglycidyl ether of a  
10 novolac resin such as ECN-1280, from Vantico Corp., at a ratio of  
11 60:20:20. Prepared on untwisted continuous filament carbon  
12 fabric or glass or Nextel<sup>R</sup> (a ceramic-based fabric), also gave an  
13 acceptable product from the standpoint of toughness and glass  
14 transition temperature.

15  
16 EXAMPLE 6. To sixty grams of PT-30 (example 2) dissolved in  
17 acetone there was added 20 grams of a diglycidyl ether of a  
18 novolac resin (PY-307 from Vantico, Inc.) and 20 grams of a  
19 polyglycidyl ether of a cresol novolac (ECN-1280 from Vantico,  
20 Inc.). The solution was catalyzed with copper acetyl acetonate  
21 and used to prepreg a carbon fabric. Following devolatizing, the  
22 prepreg was cured in a similar fashion as in example 2. This  
23 prepreg solution was also used to prepreg glass and Nextel<sup>R</sup>  
24 (a ceramic based fabric) for comparison and evaluation.

25

1       As can be seen in the above examples, there are numerous  
2 possibilities for formulating suitable cyanate resin and oligomer  
3 systems. Cyanate ester oligomers are surprisingly suitable since  
4 their glass transition temperatures can be as high as 690°F, and  
5 the glass transitions do not change drastically even after  
6 substantial modification with epoxy resins or other  
7 thermoplastics. Also, triazine polymers are inherently tougher  
8 than phenolic resins.

9       Moreover, surprisingly low resin contents of about 10% are  
10 estimated sufficient to fully encapsulate a plain weave fabric  
11 woven with continuous carbon filaments and yet maintain the  
12 toughness and integrity of the surfacing material. Typically,  
13 the very simple empirical eraser test described in example 2 on  
14 a low resin content of toughened cyanate ester cured facing sheet  
15 materials will show no broken filaments. Generally, actual road  
16 tests of transmissions employing material employing cyanate ester  
17 resins confirmed the superior performance of these materials.

18       Various adhesive formulations for bonding the cured  
19 composite to transmissions were evaluated and considered useful,  
20 as shown in Table 1. The key requirements for adhesive films at  
21 short bonding cycles of 400°F - 450°F are their capability for  
22 use at high temperatures, compatibility with friction fluids,  
23 and toughness. Modified cyanate ester resin or oligomers were  
24 found surprisingly effective for such bonding applications due to  
25 fast cure capability and lower emissions of volatized components.

TABLE 1.

WEIGHT BASED RATIOS

TRIALS	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
CATALYST	1.85	0.15	1.5	1.75	2	2	2	2	2	0.15	0.15	1.5	1.5
NBR-1411	3					3	3						
BUTVAR	18		28.5	10	10								
B-10										30			
M-30	35	30	35									30	30
PKHH		28.5		20	20	38	38	28	28	39	39	34.5	32.7
MAT GLASS							G	G					
EXL 2891	12	10								4	4	3.5	3.5
M-10				35					40				
PT-30					30	30	30	35			30		
PY-307	30	30	35	35	30	30	30	35	37	30	30	30	28
AREOSIL								3	4				
LAP SHEAR (KSI)	2140	2765	2310	2200	2475	1930	2495	1975	2170	2735	2515	1896	1775
AEROSIL : amorphous, fumed silica - Degussa Corp.													
B-10 : bisphenol A dicyanate - Lonza Corp.													
M-10, M-30 : methylene bis-(3,5-dimethylphenyl-cyanate) - Lonza Corp.													
NBR-1411 : acrylonitrile-butadiene copolymer - Zeon Chemical Inc.													
PT-30 : polycyanate ester of novolac phenol - Lonza Corp.													
PY-307 : diglycidyl of novolac phenol - Vantico Inc.													
PKHH : {phenol 4,4'-(1-methylethylidene) bisphenol with (chloromethyl) oxirane} (Phenoxy Associates).													
BUTVAR : polyvinyl butyral.													
CATALYST : Cu acetyl acetate in nonyl phenol.													
EXL 2891 : high molecular weight butadiene/acrylonitrile/styrene - Rohm & Haas.													